HW-28711

Subject Category: PHYSICS

UNITED STATES ATOMIC ENERGY COMMISSION

RADIOCHEMICAL STUDIES ON THE ISOTOPE PLUTONIUM-241

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July 14, 1953

Hanford Atomic Products Operation
Richland, Washington

Technical Information Service, Oak Ridge, Tennessee

Date Declassified: January 9, 1956.

~~Printed in USA, Price 30 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.~~

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Technical Section
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Operated for the Atomic Energy Commission by the
General Electric Company under Contract # W-31-109-Eng-52

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INTRODUCTION

A large number of plutonium isotopes have been prepared and studied during the course of the Manhattan project and subsequent operations. Plutonium isotopes from mass 232 to 243 have been characterized and their radiations measured. Of these isotopes, the group of mass 238 to 242 are of particular importance due to their production in appreciable quantities by neutron irradiation of uranium in chain-reacting piles. The investigation of plutonium-238, -239, and -240 has been intensively pursued, however relatively little work has been reported on plutonium-241. Since this isotope is the third most abundant in pile produced plutonium, its study with regard to its production and radioactive characteristics is highly desirable.

A knowledge of the isotopic composition of pile produced plutonium is of importance to pile operation, the determination of the specific activity of pile produced plutonium, and the determination of effective pile cross sections. Furthermore, since the isotopes of americium and curium grow into irradiated uranium through the decay of plutonium-241, the abundance of the heavy transuranics may be predicted from plutonium-241 contents and a knowledge of the half-life. In connnection with a program involving isotopic abundances and analysis, the present investigation was initiated to obtain analytical methods for the determination of plutonium-241 and to determine its occurrence in plutonium produced in the Hanford Piles.

SUMMARY

A method for the determination of small amounts of americium in plutonium was developed. The half-life of plutonium-241 was measured by following the growth of its americium daughter into a plutonium sample of known isotopic content and found to be 14.2 ± 1 years. The production

of plutonium-241 in the piles was studied as a function of neutron exposure and isotope content by similar techniques and the results correlated with other pertinent data.

EXPERIMENTAL APPROACH

Two previous studies of isotope production in the pile have been made which deal with plutonium-241. Larrick[1] studied, from a theoretical standpoint, the build-up of the various isotopes as a function of the several operating parameters of the pile. Using the best nuclear data available to him in 1949, he calculated the amount of the isotopes produced in the range from zero to 600 MWD/T (megawatt days per ton of uranium). In view of the considerable uncertainty in the values of the nuclear and pile constants used in the calculation, experimental verification was highly desirable.

The Argonne National Laboratories have made a number of determinations of plutonium-241 contents in plutonium by mass spectrographic and beta counting techniques.[2,3] In one report the production of this isotope as a function of pile exposure was studied. The isotopic ratios which were determined by these methods were confirmed by this investigation. The exposure values cited in this report, however, were uncertain in a high degree.

The beta half-life of plutonium-241 has been variously reported as 10, 14.2, and 13.0 years. The earliest estimate was the 10 year figure quoted by Seaborg[4] in 1948. A later determination was made at the University of California Radiation Laboratories by following americium growth into a plutonium sample of known isotopic content. The value found was 14.2 ± 1 years.[5] Very recently, Mackenzie, Lounsbury, and Boyd have reported a value of 13.0 + 0.2 years,[6] determined by following americium growth into a sample of plutonium which had been analyzed for plutonium-241 by mass spectrographic techniques. The americium determinations were made by alpha energy analysis.

Since the half-life of plutonium-241 enters into the calculation of its abundance in the method developed in this report, it was desirable to determine this value independently in order to permit the choice of one of the two most recent measurements.

The experimental approach to the determination of the half-life and abundance of plutonium-241 was based on measurement of the growth of the isotope americium-241, which results from the decay of plutonium-241. The mathematical expression of this method may be readily derived from the classical laws of radioactive decay. If N_o is the initial number of atoms of Plutonium-241 present at the start of a decay period, and λ is the decay constant of the isotope, then the number of atoms remaining after time t is given by the equation

$$N = N_o e^{-\lambda t}$$

If the half-life of the daughter activity, in this case americium-241, is very much larger than that of the parent, then the decay of the daughter may be neglected over several half-lives of the parent and the number of atoms of daughter formed will be equal to the difference between N_o and N. Rearranging:

$$N_{Am} = N_o(1-e^{-\lambda t})$$

It follows that if the amount of americium grown into a sample of known N_o is determined after a time t, the decay constant and hence the half-life may be calculated. Similarly if the half-life is known, the equation may be solved for N_o and a determination of the amount of americium grown into a separated sample in a known time suffices to determine the amount of parent plutonium-241 present.

The above expressions are in terms of the number of atoms of isotopes. In the actual investigations, the quantities of each isotope present were invariably determined by measurements of their activity with

standard counting equipment. The number of atoms giving rise to a given activity in terms of disintegrations per unit time, is given by

$$N = A/\lambda$$

where A is the activity in d/m/gm and N is the number of atoms. In the case of the isotopically pure americium 241 which results from the decay of plutonium-241, λ has an unambiguous value. Plutonium, however, is a mixture of isotopes of differing half-lives and the decay constant for a mixture is consequently dependent on the exact isotopic composition of the particular sample. For this reason, it was necessary to carry out complete isotopic analyses of each plutonium sample studied before calculation of the percentage abundance of the 241 isotope.

The present investigation depended throughout on sensitive and accurate americium analyses. The methods previously developed were examined and found to be in general inadequate for the purposes contemplated. Accordingly, a new method for the quantitative separation of americium and plutonium was developed and used throughout the work.

ANALYTICAL METHODS

A number of analytical methods were used in the various investigations reported. In addition to the usual counting techniques for the determination of alpha activity, a precipitation method developed previously was used for the standardization of americium solutions. Pulse analysis techniques were also used for the determination of americium and the determination of plutonium-238 isotopic content. A fission counting method was used for the determination of plutonium-240.

The methods and techniques of precise radiometric assay are too well known to require detailed discussion. An excellent discussion of the problems of sample preparation for this type of measurement has been given by Huffard and Scott.(7) The counting instrument used throughout this work was of the "alpha proportional" type described by Simpson.(8)

An americium method devised by Miller[9] and modified by the author[10] was used for the preparation and standardization of americium solutions for the development of the americium method reported later. Miller's method is based on the selective oxidation of plutonium to the hexavalent state and the subsequent precipitation of trivalent americium with cerium fluoride carrier. Ceric salts are the oxidant in this procedure. The mixture to be analyzed for americium is treated for 15 minutes at 85 C with ceric sulfate. Americium is not oxidized under these conditions. The small quantity of ceric ion that is reduced to the trivalent state during the oxidation is then precipitated by the addition of hydrofluoric acid to the sample. Isomorphous americium trifluoride is co-precipitated, or "carried", on the cerium precipitate and is subsequently centrifuged out of solution. The precipitate is washed repeatedly with nitric and hydrofluoric acid to remove hexavalent plutonium and then dissolved with zirconyl ion. The cerium and americium are reprecipitated with excess hydrofluoric acid, centrifuged, and washed as before. The second precipitation serves to free the americium from the traces of plutonyl ion adsorbed or occluded by the galatinous fluoride of cerium. Finally, the washed precipitate is slurried and transferred to a platinum disc for alpha counting. A schematic outline of the procedure is shown in Figure 1.

This method has been widely applied to a number of different analytical systems and is capable of excellent results with the most careful attention to details. The accuracy of the method has been stated to be 100% and the precision of a single determination ± 4.6% at the 95% confidence limits.

For the actual americium determination reported in this paper, a new solvent extraction method was developed and used. This technique depends on the separation of americium and plutonium by a series of extractions of the chelate compounds of these two elements which are formed with thenoyltrifluoroacetone (TTA)[11] under carefully controlled

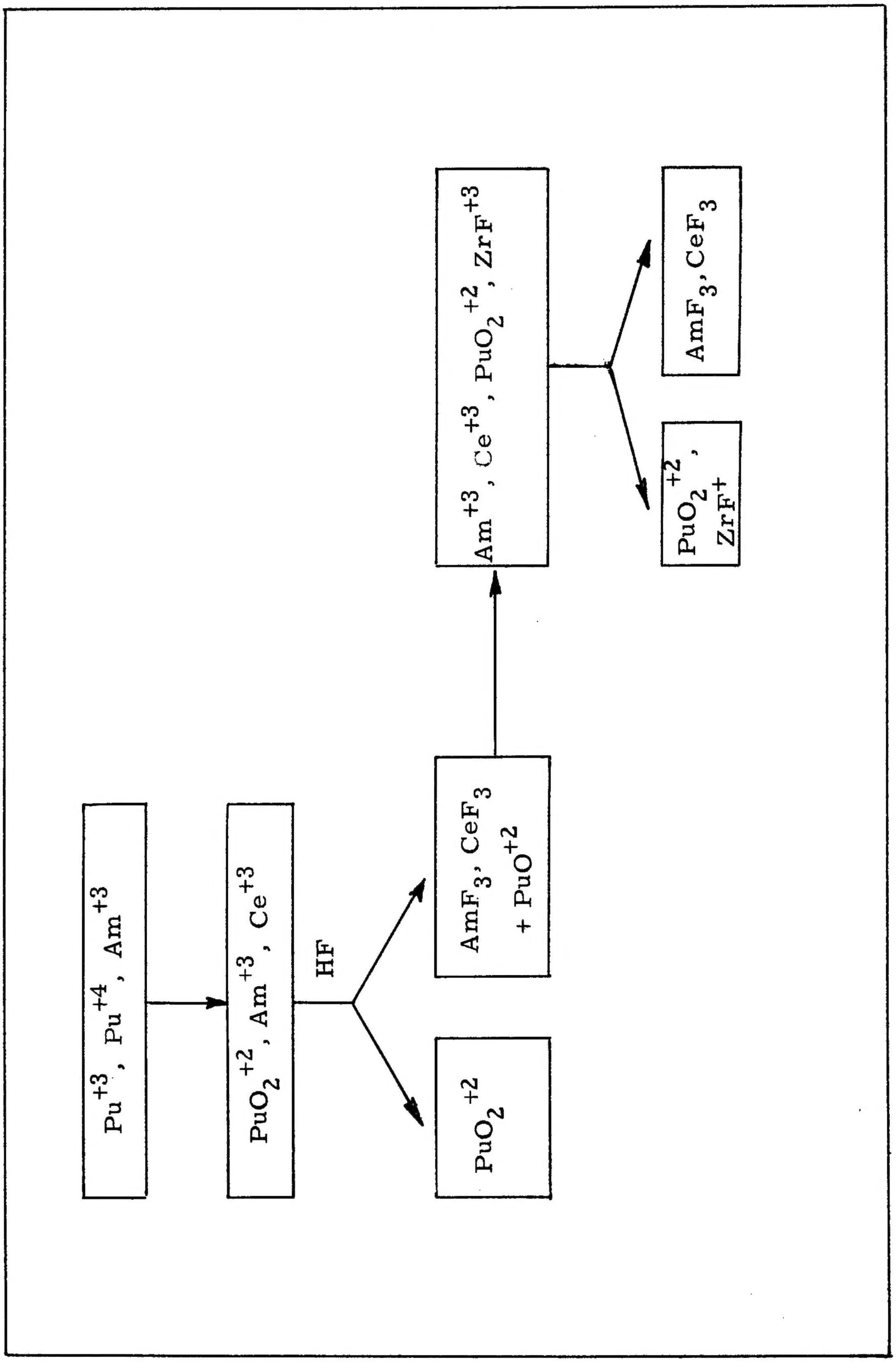


FIGURE 1

Modified Cerium Fluoride Method for the Determination of Americium

pH. Plutonium is first reduced to the tri- or tetravalent state with hydroxylamine. The pH is adjusted to about 4.8 with an acetic acid - acetate buffer and the mixture extracted with a solution of TTA in benzene. Americium is separated from plutonium by an aqueous extraction of the organic solution with 0.5 M nitric acid, the plutonium remaining in the organic phase. An aliquot of the final aqueous phase is then mounted for alpha counting in the usual manner. A schematic diagram of the analysis is shown in Figure 2.

The accuracy of this method relative to the cerium fluoride technique has been determined to be 100.9% and the precision of a single determination has been found to be ± 2.6% at the 95% confidence limits.

The characteristic alpha energies of the various isotopes of plutonium and americium may be made the basis of an analytical method for americium in plutonium or for the determination of plutonium-238 in pure plutonium. Americium-241 and plutonium-238 have alpha particle energies of 5.48 and 5.49 mev respectively, while plutonium-239 and 240 have alpha energies of 5.15 and 5.16 mev.[12] These two pairs may be separated by suitable pulse analysis instruments and their relative activities measured.

In the equipment used in this investigation, the alpha particles from a thin source were allowed to expend their full energy in a total ionization chamber, producing a pulse whose magnitude was proportional to the energy of the alpha particle. The output of the chamber and associated preamplifier was fed to a stable pulse height discriminator circuit of the type described by Fairstein[13] and analyzed in terms of their height. The entire range of pulse heights was scanned and the counting rate displayed as a function of pulse height, and consequently of alpha energy. The resulting spectrum was analyzed for either americium or plutonium-238 and the activity ratios computed from this data. A block diagram of the equipment is shown in Figure 3.

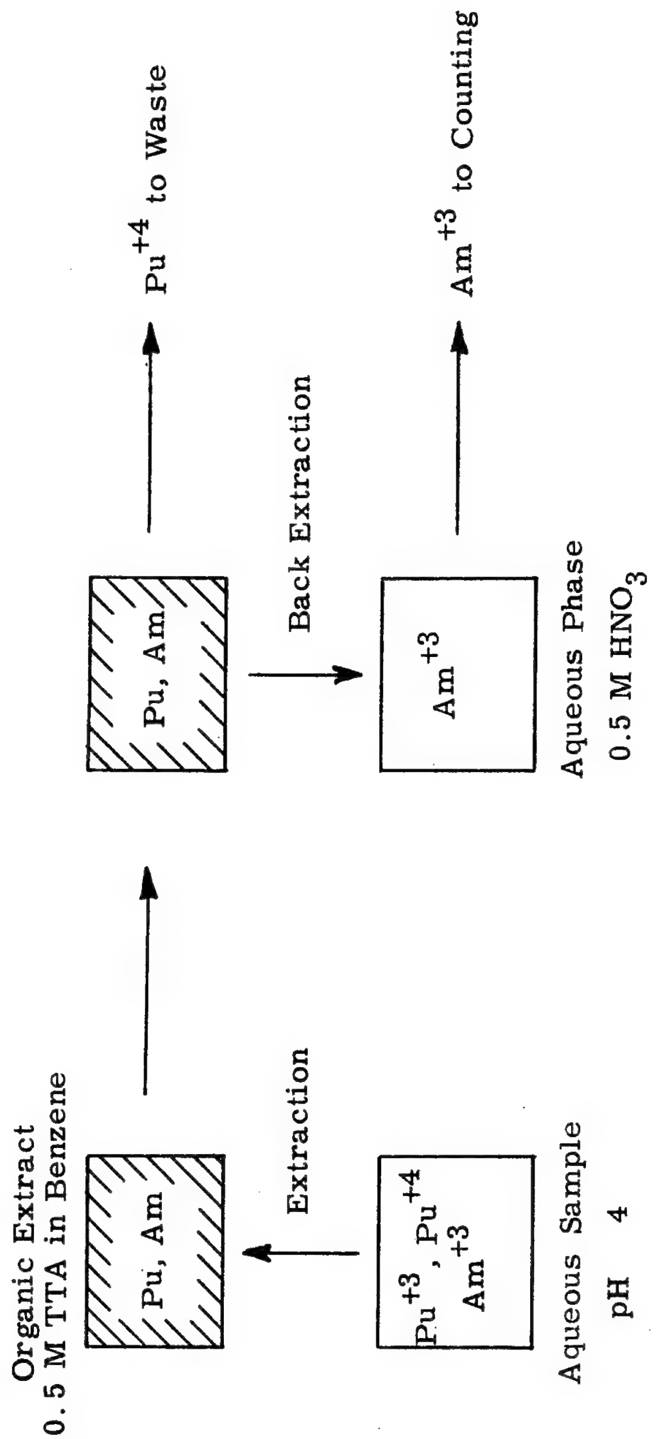


FIGURE 2

TTA Method for the Determination of Americium

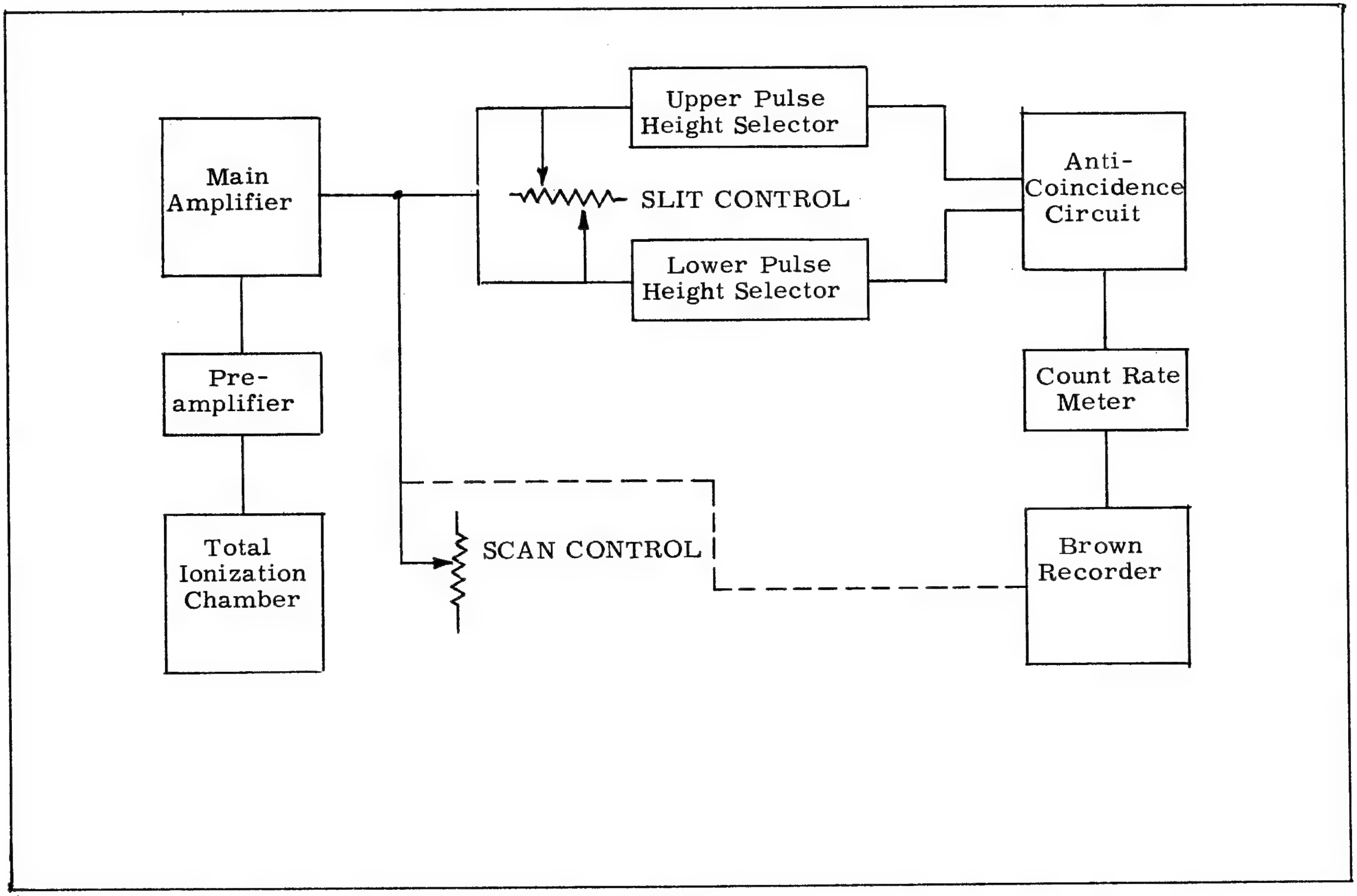


FIGURE 3

Block Diagram of the Alpha Energy Analyzer

A typical scan of counting rate as a function of alpha energy for a mixture of plutonium isotopes is shown in Figure 4. The plutonium-239 and 240 are not resolved by the instrument, however the plutonium-238 peak may be clearly distinguished. In the determination of activity ratios from such scans, the ratio of peak heights was taken equal to the ratio of activities of the species in question.

A second spectrum is shown in Figure 5 and indicates the application of the instrument to the determination of americium and plutonium in their mixtures. The activity ratio of americium to plutonium is again calculated directly from peak-height ratios after a small correction of the americium peak for the plutonium-238 contribution.

The precision and sensitivity of the pulse analysis technique were not sufficient for the determination of americium in the solutions investigated, however the method served as a semi-quantitative method for a number of confirmatory analyses, especially valuable in separations studies.

A knowledge of the plutonium-240 content of the plutonium samples used in this study was necessary for the calculation of the specific activity of the plutonium. The analysis for the 240 isotope was based on the high spontaneous fission rate of this isotope in comparison with the other isotopes present. The spontaneous fission rate of plutonium-240 has recently been determined to be 1.51×10^6 fissions/gram/hour,(14) while the rate for plutonium-239 is only 36 f/g/hr.(15) The spontaneous fission rate of plutonium-238 is comparable to that of plutonium-240, being 5×10^6 f/g/hr,(16) however the low abundance of this isotope in the material studied made its contribution small. In principle, the spontaneous fission rate of a plutonium sample was measured in a specially designed counter capable of counting a few fission events per hour in the presence of 10^9 alpha disintegrations per minute. From the measured spontaneous fission rate of the sample and its weight, the plutonium-240 content could be calculated. In actual practice, it proved to be convenient to "weigh" the

FIGURE 4

Alpha Spectrum of a Plutonium Sample

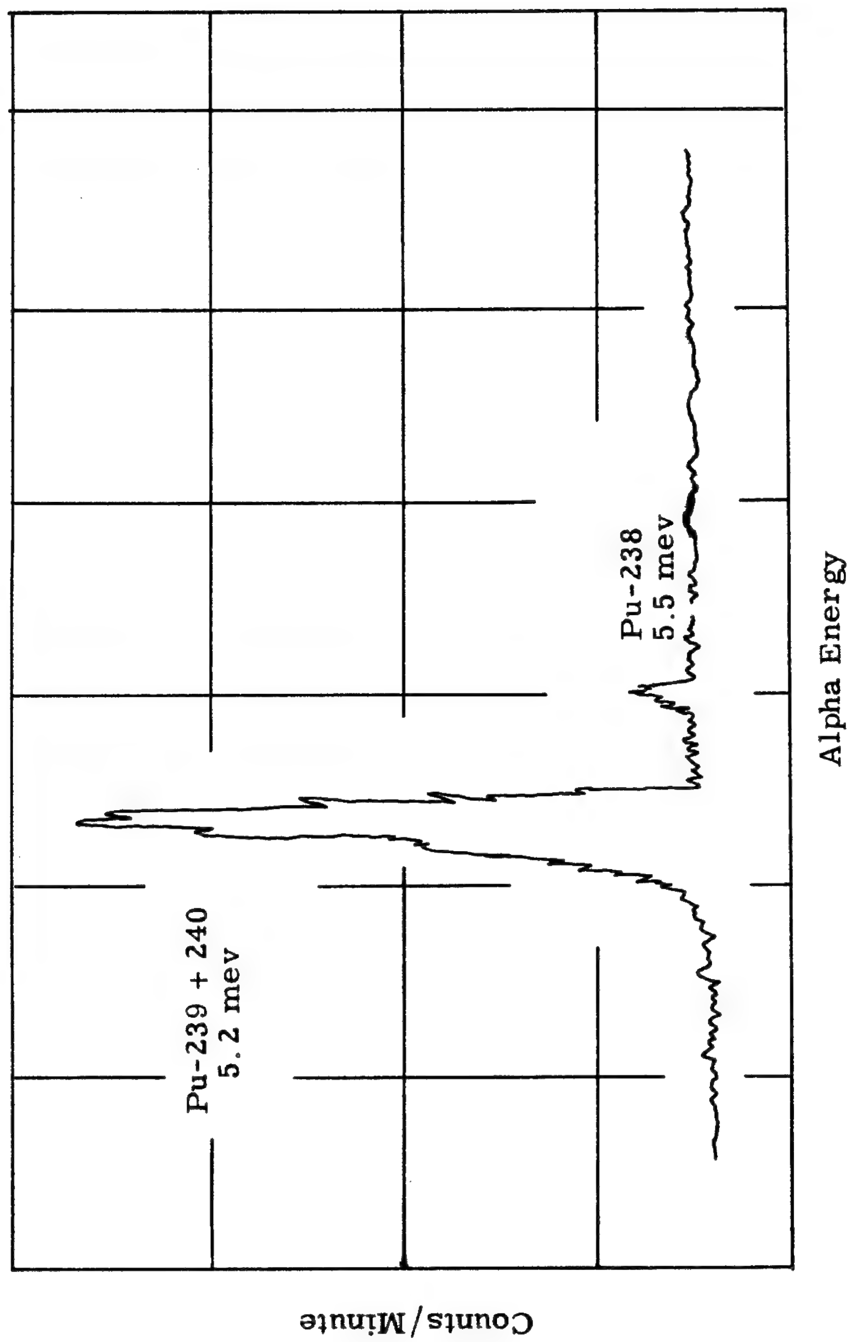
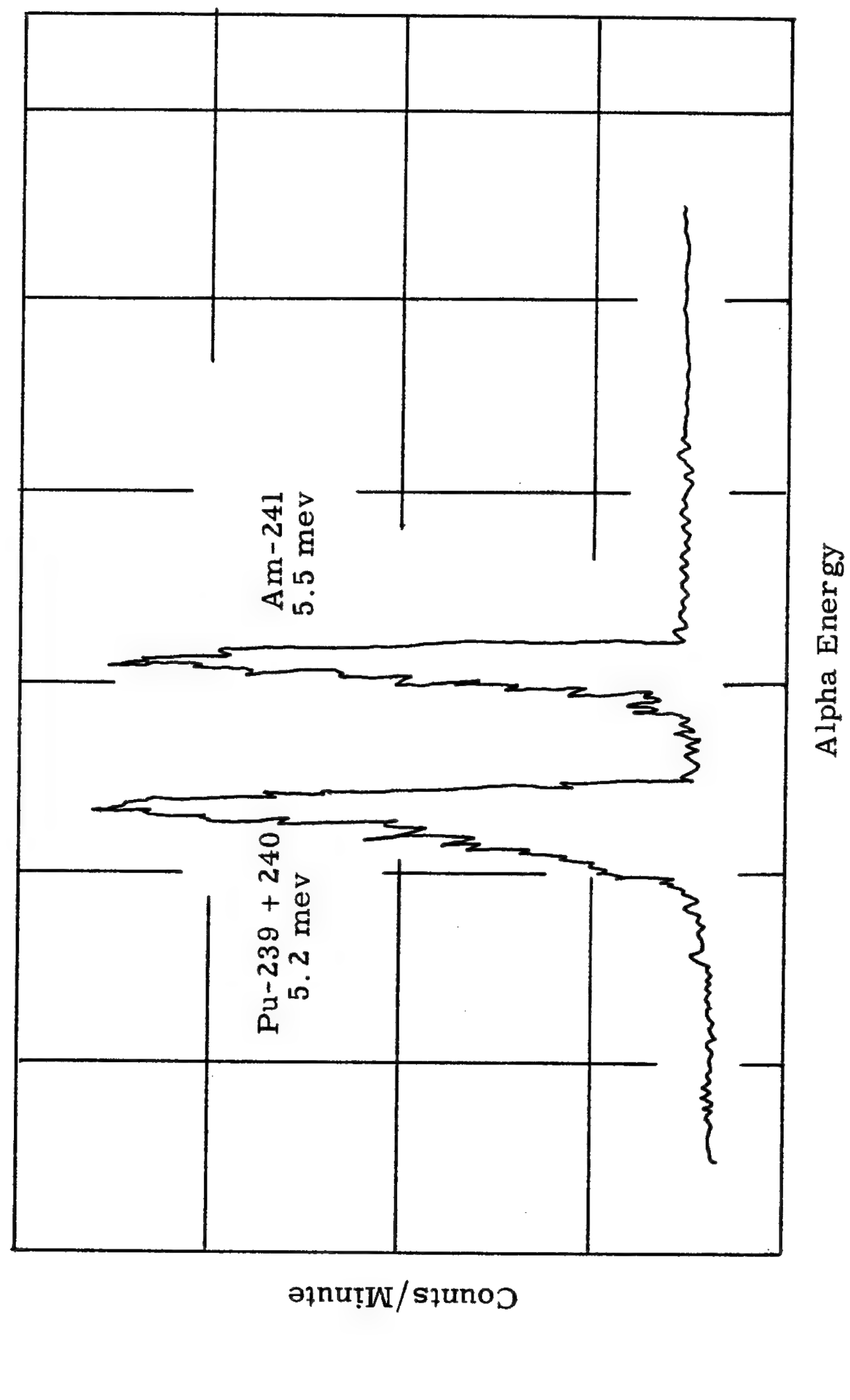


FIGURE 5

Alpha Spectrum of a Plutonium and Americium Sample



sample by irradiating it with thermal neutrons and measuring the induced fission rate due to plutonium-239. The equipment was standardized with a plutonium sample of known isotopic composition and an empirical equation developed relating plutonium-240 content in weight per cent to the experimental ratio of induced to spontaneous fission rate.[17]

The uncertainties in the per cent of plutonium-240 measured by this method amount to about 1% in most cases. This results in an uncertainty of about 0.1% in the specific activity calculated from such data.

Plutonium-241 was determined by measurement of the amount of americium grown into purified plutonium samples in a known length of time through the decay of plutonium-241. The fundamental decay equation has been given in the section on experimental approach. The conversion of this equation to one in terms of measured activities is given in detail by the author.[18] The form of the equation used to calculate Pu-241 from measured activities is:

$$\text{wt \% Pu-241} = \frac{239}{241} \cdot \frac{(c/m)\text{Am}}{(c/m)\text{Pu}} \cdot \frac{1}{R} \cdot \frac{1}{(1-e^{-\lambda t})} \cdot \frac{T_{1/2}\,\text{Am}}{T_{1/2}\,\text{Pu}}$$

where

$T_{1/2}$ Am = half-life of americium-241

$T_{1/2}$ Pu = half-life of plutonium-239

(c/m)Am = observed americium counting rate

(c/m) Pu = observed plutonium counting rate

R = ratio specific activity Pu-239 to specific activity of plutonium studied

λ = decay constant of Pu-241

t = time elapsed since last separation of Pu from Am

The plutonium activity of the sample was determined by a direct measurement of total alpha activity, from which the experimental americium activity was subtracted. The specific activity term was calculated from the measured isotope ratios.

EXPERIMENTAL PART

TTA Method for the Determination of Americium

The reaction between a metal ion of charge + n and the chelating agent thenoyltrifluoroacetone (TTA) may be written as

$$M^{+n} + nTTA \rightleftharpoons M(TTA)_n + n\,H^+$$

for the simplest case of complete chelation and no side reactions. The equilibrium constant for this reaction is

$$K = \frac{[M(TTA)_n]}{[M^{+n}]} \qquad \frac{[H^+]^n}{[TTA]^n}$$

In the presence of an organic phase in which the unchelated metal ion is insoluble and the chelated ion very soluble, the chelate will distribute itself between the organic and aqueous phase with a distribution constant D, the ratio of the concentration of the chelate in the organic phase to that in the aqueous phase. If this distribution constant is very large, as is the case for the TTA-metal compounds, the metal chelate will occur to an appreciable extent only in the organic solution. If the organic phase is a non-polar solvent such as benzene, the metal ion is almost insoluble in the organic and likewise will occur to an appreciable extent only in the aqueous phase. Under these conditions, the term

$$\frac{M\,(TTA)_n}{M^{+n}}$$

may be replaced by a distribution constant for the metal, d, defined as the ratio of the metal concentration in the organic phase to that in the aqueous. The equilibrium constant for the two-phase system then becomes

$$K = d\,\frac{[H^+]^n}{[TTA]^n}$$

Rearranging, the metal distribution constant may be expressed as

$$d = K \left[TTA\right]^n \cdot \frac{1}{\left[H^+\right]^n}$$

It follows from these considerations that the distribution constant for the metal is proportional to the nth power of the TTA concentration and inversely proportional to the nth power of the hydrogen ion concentration. If the equilibrium constant for two metals, K, are sufficiently different from one another, it may be seen from the form of the distribution constant equation that the possibility for separation exists by extraction into an organic phase at controlled pH. A series of experiments were accordingly carried out to establish the feasibility of this approach for the quantitative separation of americium and plutonium.

In order to uncover reaction rate effects which might be of importance in further studies, a series of measurements were made of the rate of extraction of americium by a benzene solution of TTA. A standard solution of pure americium-241 was prepared by dilution in 2 N HNO_3 and known amounts taken for extraction. The pH was adjusted to about 5 with NaOH and the resulting sample diluted to 1.0 ml. The aqueous solution was then contacted for various lengths of time with 1.0 ml of a 0.5 M solution of TTA in benzene. The extractions were carried out in test tubes held just outside the radius of rotation of an electrically driven bar magnet. A small stainless steel strip in the test tubes served as an agitator. After extraction the phases were allowed to separate and an aliquot of the organic phase taken for analysis. The total amount of americium found in the organic layer was calculated and compared to the total amount present in the system. The results are shown in Table 1.

TABLE I

The Extraction of Americium as a Function of Time

pH 5. 0.5 M TTA in Benzene

Extraction time, minutes	Am in organic counts/min	Am, total, counts/min	Am extracted %
2	1317	1291	101
2	1272	1291	98
5	1250	1291	97
5	1304	1291	101
10	1288	1291	100
10	1307	1291	101
15	1344	1291	103
15	1250	1291	97

From these results it was concluded that the extraction of americium under these conditions is very rapid. In order to provide a sizeable margin of safety with respect to extraction time, all subsequent extractions were carried out for fifteen minutes.

The extraction behavior of americium as a function of pH was studied by taking known amounts of the americium standard and adjusting the pH to the desired value by the addition of NaOH. The adjusted solution was then diluted to 1.0 ml and the pH measured with a carefully standardized Beckman Model G pH meter, using micro electrodes. The solution was then contacted for fifteen minutes with 1.0 ml of 0.5 M TTA in benzene. At the end of the extraction, the phases were allowed to separate and an aliquot of the organic phase taken for analysis. Above pH 3.8 the pH was found to change during extraction and 50 μl of a 2 N sodium acetate solution were added before dilution to act as a buffer. The results of these experiments are shown in Table 2 and Figure 6.

FIGURE 6

Extraction of Americium as a Function of pH

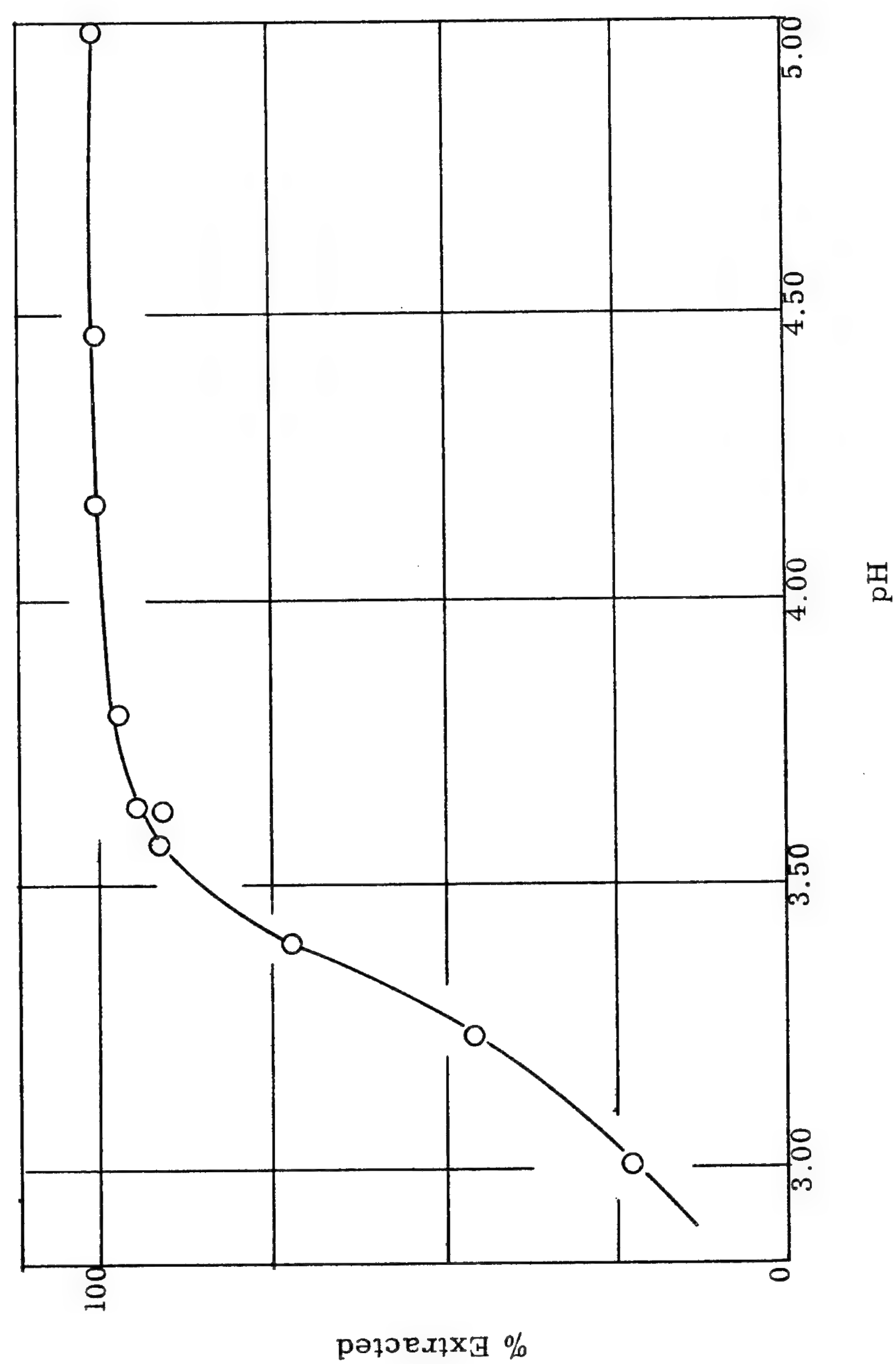


TABLE II

The Extraction of Americium as a Function of pH

0.5 M TTA in Benzene. 15 min extraction

pH	Am in organic counts/min	Am taken counts/min	Am extracted %
3.01	295	1316	22
3.23	599	1316	46
3.39	943	1316	72
3.57	1169	1316	89
3.64	1139	1316	87
3.66	1204	1316	92
3.79	1240	1316	95
4.16	1321	1316	100
4.46	1311	1316	100
5.00	1319	1316	100

These data are in good agreement with the results of Werner[19] and with the shape of the theoretical curve for a trivalent metal.

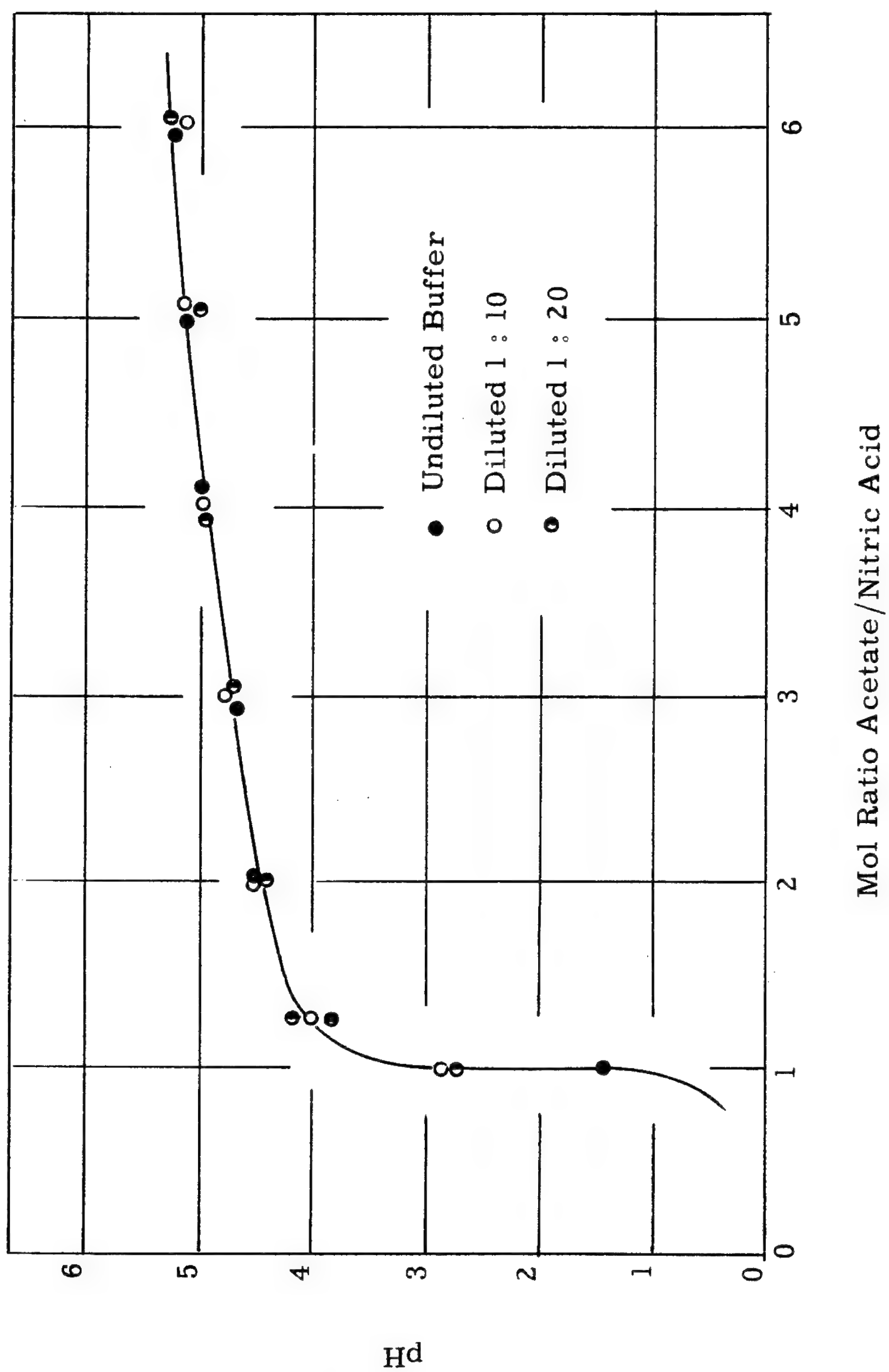
Since the extraction of americium is critically dependent on the pH of the aqueous system, an acetic acid-acetate buffer system was investigated for application to these systems. The buffer system was generated by the direct addition of sodium acetate to nitric acid solutions.

A series of determinations of the pH of aqueous systems resulting from the addition of sodium acetate to nitric acid were made. Various mol ratios of acetate to acid were made up at three dilutions and the pH of the solution measured. The resulting "titration curves" are shown in Figure 7.

A comparison of these data with Figure 6 indicates that the proper pH for quantitative extraction of americium may be obtained by the direct addition of sodium acetate to nitric acid solutions of americium in a ratio of two moles of acetate per mole of acid. Such addition is a convenient and accurate way of adjusting the pH before extraction.

FIGURE 7

Sodium Acetate - Nitric Acid Buffer



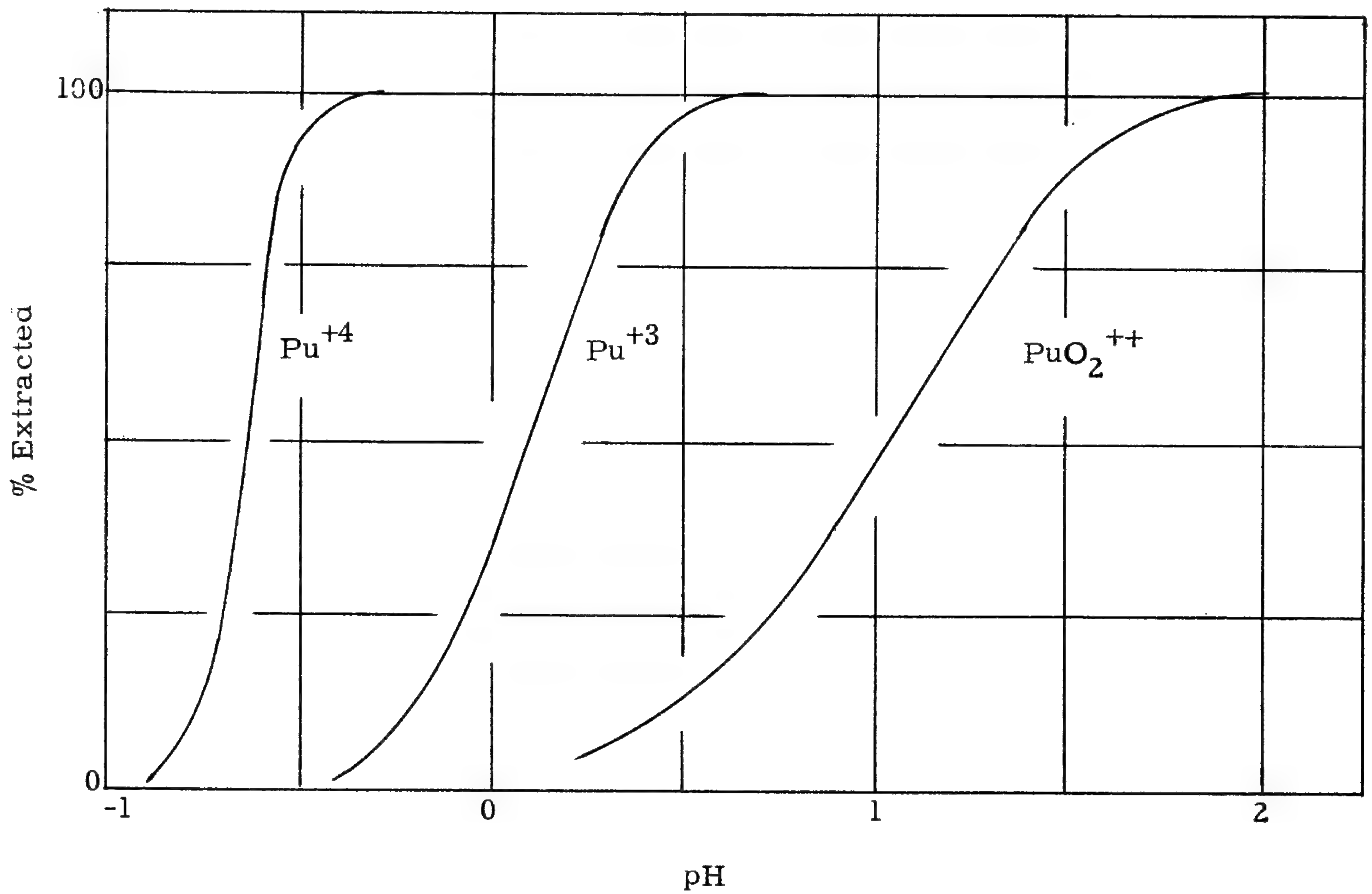
The behavior of plutonium in TTA extractions has been studied by a number of workers[20, 21]. While several experiments were carried out to check the published data, no systematic investigation of the extraction of plutonium was undertaken. The success of the method as developed and the large body of experience collected in its application amply substantiate previous results. These data which were drawn from several sources, are summarized graphically in Figure 8, and have been computed from the published data to apply to the present conditions.

A consideration of the information of Figure 8 indicates that all the plutonium species would be expected to extract at a pH sufficiently high to extract americium. Several factors, however, tend to decrease the amount of each species actually found to extract into benzene-TTA solution at pH of about 5. Plutonium III is markedly unstable at high pH values, and is slowly oxidized to the tetravalent state[22]. Plutonium VI is likewise unstable in the presence of easily oxidized organics and so will occur to a smaller extent in the absence of a holding oxidant. Finally, plutonium IV polymerizes rapidly at pH above 2 to yield an unextractable species[23]. All of these factors tend to decrease the amount of plutonium extracted with americium.

In spite of these effects the majority of the plutonium in most samples is extracted into the organic phase with americium. Final separation must be accomplished, therefore, by "back-extracting" americium into a second aqueous phase under conditions such that plutonium will remain in the organic layer. A consideration of the extraction curves for plutonium indicates that 0.5 M nitric acid fulfills this requirement in the absence of plutonyl ion. The behavior of plutonyl ion in the analytical scheme was investigated by carrying out the analysis on a standard solution of americium and plutonium known to contain about 40% of the total plutonium as plutonium VI. The analysis was carried out (1) with no treatment of the sample before extraction, (2) with the addition of sodium dichromate as a holding oxidant for the plutonyl ion, and (3) with the addition of

FIGURE 8

Extraction of Plutonium as a Function of pH



hydroxylamine to reduce the plutonium to the tetravalent and trivalent states before extraction. The results are summarized in Table 3.

TABLE III

The Behavior of Plutonium VI in the Americium Analysis

0.5 M TTA in Benzene. pH 4.8. Extraction 15 min

Sample treatment	Activity found counts/min	Am taken counts/min	Am Recovery %
None	1856	1364	136
	1809	1364	133
50µl 0.1 N $Na_2Cr_2O_7$	5031	1753	287
	4436	1753	253
50µl 5.0 M NH_2OH	2198	2196	100
	2192	2196	100

It is seen that the expected interference due to plutonyl ion may be effectively eliminated by the addition of hydroxylamine to the sample before extraction.

The method adopted was as follows:

1. Pipet the desired aliquot of the sample to be analysed for americium into a test tube and rinse the pipet twice with 2 N sodium acetate. Add 50 µl of 5 M hydroxylamine to the solution. Dilute to about 1.0 ml with distilled water.

2. Pipet 100 µl of 0.5 M TTA in benzene into the test tube and extract for fifteen minutes.

3. Transfer 500 µl of the organic layer to a second test tube containing 500 µl of 0.5 N nitric acid. Rinse the pipet with about 500 µl of fresh TTA - benzene solution and extract for fifteen minutes.

4. Remove an aliquot of the 0.5 M nitric acid containing the americium and mount on a platinum disc for counting.

The extent of separation of americium from plutonium was determined in several ways. A direct determination of plutonium in americium separated by the above procedure was made by alpha energy analysis. No indication of plutonium contamination was observed. More sensitive experiments carried out by analysis of the final aqueous solution for plutonium indicated less than 0.001% of the plutonium is recovered with the americium. The value quoted is the detection limit of the procedure used.

The precision and accuracy of the method were established in a series of determination on a standard mixture of americium and plutonium whose composition had been carefully measured by the cerium flouride and alpha energy analysis methods. A total of 22 americium analyses were made on two such standards. The results are shown in Table 4.

TABLE IV

Precision and Accuracy of the TTA Method for Americium

0.5 M TTA in Benzene, pH 4.8, Extracted 15 min

Standard	Am found counts/min	Am taken counts/min	Recovery %
A	27541	27303	100.9
	27913	"	102.2
	27663	"	101.3
9.672×10^6	27029	"	99.0
c/m/ml Pu	27045	"	99.1
2.730×10^6	27990	"	102.5
c/m/ml Am	26924	"	98.6
	27793	"	101.8
	26840	"	98.3
	27529	"	100.8

TABLE IV (contd.)

Standard	Am found counts/min	Am taken counts/min	Recovery %
B	2264	2239	101.1
	2261	"	101.0
	2280	"	101.8
3.03×10^7	2290	"	102.3
c/m/ml Pu	2276	"	101.6
1.119×10^6	2242	"	100.1
c/m/ml Am	2227	"	99.4
	2223	"	99.3
	2250	"	100.5
	2254	"	100.7
	2272	"	101.5
	2265	"	101.2

The accuracy of the method was found to be 100.7 %. The precision of the method, based on 22 determinations was found to be ± 2.6% for a single determination at the 95% confidence limits.

The Determination of the Beta Half-life of Pu-241

The growth of americium into a carefully purified sample of plutonium was measured as a function of time, in order to establish the rate of growth from which the half-life of plutonium-241 can be calculated.

The plutonium sample used in this experiment was supplied by the University of California Radiation Laboratories and designated by them as CA-6 plutonium. Its isotopic composition was determined by mass spectrographic analysis. The results of this analysis, which was carried out on August 28, 1952, are shown in Table 5[24]. The precision values given are average deviations.

TABLE V

Mass Spectrographic Analysis of CA-6 Plutonium

Isotope	Abundance mol %	Precision (average deviation) mol %
Pu-239	30.39	0.2
Pu-240	49.39	0.4
Pu-241	13.46	0.1
Pu-242	6.75	0.1

The sample was purified from americium by a solvent extraction procedure using TTA as an extractant. The separation procedure is summarized in Figure 9. An aliquot of the plutonium solution as received was transferred to a test tube and diluted to 1.0 ml with 1 N nitric acid. The plutonium was reduced by treating the sample with 150 µl of 5 M hydroxylamine for 15 minutes at 85 C. The reduced solution was then treated with sodium nitrite to destroy excess reducing agent and to oxidize the plutonium to the tetravalent state. Americium is not oxidized by this treatment and remains in the trivalent state. The solution was then contacted for 15 minutes with 1.0 ml of 0.5 M TTA in benzene and the plutonium extracted almost quantitatively into the organic phase. The organic layer was then extracted with three successive 1.0 ml portions of 0.5 N nitric acid to remove any traces of americium which might have been carried into the organic phase with plutonium. This procedure has been shown to quantitatively remove americium. Finally, the plutonium was extracted into an aqueous phase 2 N in sulfuric acid and 1 M in hydroxylamine. This aqueous solution was washed repeatedly with benzene to remove traces of organic matter and then diluted 10 ml with 1 N nitric acid. The resulting solution was 0.9 M in HNO_3, 0.1 M in H_2SO_4, 0.05 M in NH_2OH and 0.05 M in HCl. The total activity of the solution immediately after separation was determined to be 7.94×10^4 c/min/100 µl.

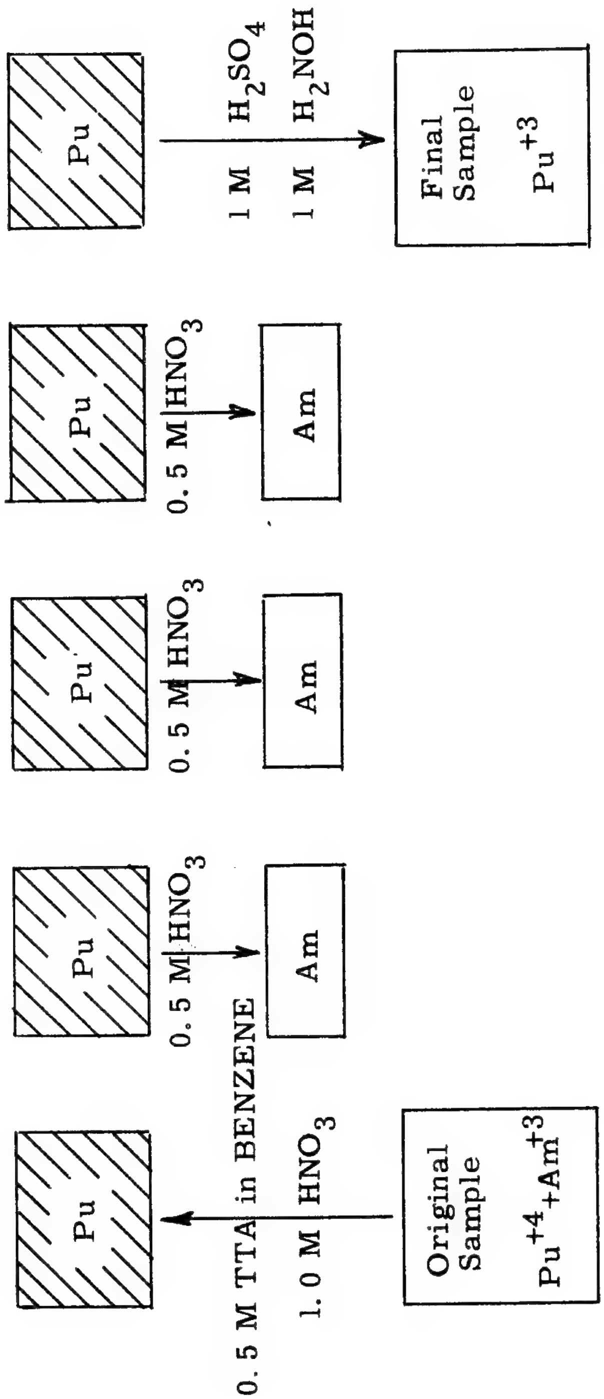


FIGURE 9

Separation of Plutonium from Americium

At several times after purification of the plutonium, 100 μl aliquots of the sample were taken for americium analysis. The determinations were made by the TTA method described previously. Each determination was made in octuplicate. In order to establish the recovery of americium, an additional determination was made with 100 μl aliquots of the plutonium solution under study plus 25 μl aliquots of a pure americium solution of known activity. The recovery of the added americium activity was 100% within the precision of the determination. The counting instruments were carefully standardized against known sources before each determination. The results of the americium analyses are shown in Table 6.

TABLE VI

Determination of Americium Grown into Separated Plutonium

Total plutonium = 7940 c/min

Determination no.	Time since separation days	Am found c/min	Average Am c/min
1	0.01	0.3	0.0
		0.5	
		-0.2	
		0.3	
		-0.2	
		-0.5	
		-0.1	
		0.0	
2	10.8	24.8	26.8
		25.4	
		27.3	
		26.2	
		27.5	
		28.7	
		27.9	
		26.2	

TABLE VI (contd.)

Determination no.	Time since separation days	Am found c/min	Average Am c/min
3	27.9	73.1	77.8
		77.8	
		80.2	
		79.8	
		79.1	
		76.7	
		76.9	
		78.6	
4	53.9	137.0	138.6
		139.9	
		138.5	
		136.6	
		140.5	
		139.6	
		137.8	
		138.9	

These results are shown graphically in Figure 10. The data are seen to follow the straight line relationship expected for growth times short with respect to the half-life of the parent isotope. The slope of the line is 2.63 ± 0 21 counts per minute per day.

The half-life of plutonium-241 was calculated from the measured slope, the total plutonium counts per minute in the aliquot taken for analysis, and the isotopic composition of the plutonium according to the equation

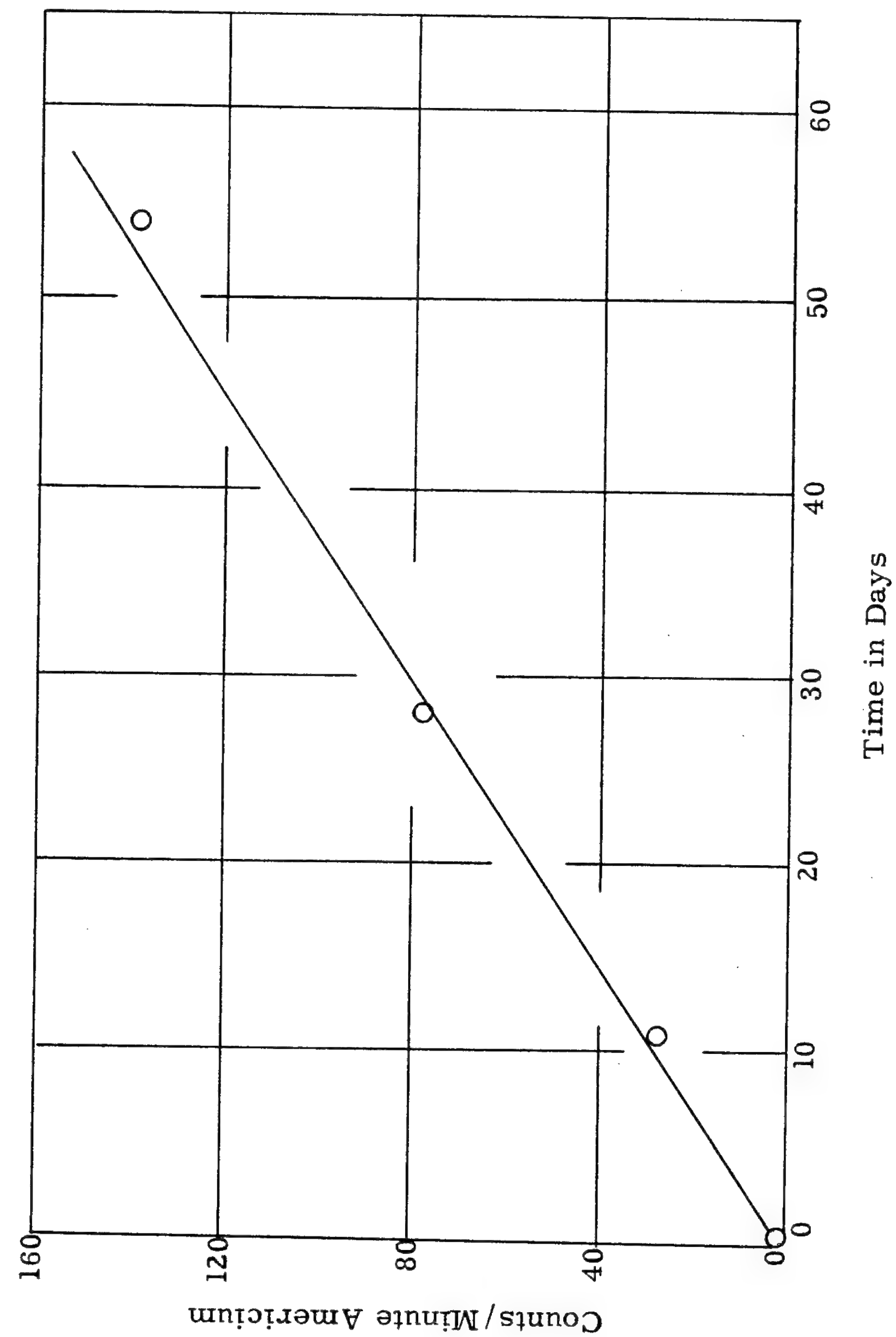
$$T_{\frac{1}{2}}\ \text{Pu-241} = \frac{\text{Sp. Act. Am}}{\text{Sp. Act. Pu}} \cdot \frac{\%\ \text{Pu-241}}{100} \cdot \frac{\text{c/m Pu}}{d\ \text{Am}/dt} \cdot \frac{\ln 2}{365.25}$$

where:

Sp. Act. Am = Specific activity Am-241 in d/min/μ mole
Sp. Act. Pu = Specific activity Pu in d/min/μ mole
% Pu-241 = mole percent Pu-241 in plutonium
c/m Pu = counts/minute plutonium in aliquots
dAm/dt = slope of Am growth curve in counts/minute/day.

FIGURE 10

Growth of Americium into Plutonium



Since an appreciable length of time elapsed between the mass spectrographic analysis and the half-life experiments, it was necessary to correct the plutonium-241 analysis for decay. A half-life of 13.0 years was used to calculate this decay. A consideration of the form of the correction shows that a 10% error in the half-life assumed for this calculation introduced only a 0.4% error in the half-life calculated from the experimental data. The first experimental half-life was then used to recalculate the decay correction and a final value recomputed from the data. In this manner, errors from the assumed half-life were reduced to negligible proportions. The contribution to the specific activity of the plutonium due to the isotope plutonium-238 was determined by pulse analysis of the plutonium and found to be 29.3 ± 2%.

The half-life for the beta decay of plutonium-241 calculated from the experimental data was found to be 14.2 ± 1.0 years.

The Determination of the Abundance of Plutonium-241 in Pile Produced Plutonium

A number of sample of pile produced plutonium with various irradiation histories were analyzed for their plutonium-241 content by determining the amount of americium grown into them in a known length of time. The plutonium samples were selected from routinely processed material which had been irradiated to exposure values of from 55 to 700 MWD/T (megawatt days per ton of uranium). An attempt was made to choose samples from the later part of a large batch of similar material in order to reduce isotopic contamination due to process hold-up and recycled plutonium to a minimum. The samples were received as plutonium nitrate solutions and contained no americium initially.

After a known period of decay, which varied from 100 days to several years, aliquots of the samples were taken for americium analysis by the TTA method described previously. The plutonium concentration of samples was measured directly. The experimental data is shown in Table 7. All analyses were made in quadruplicate.

TABLE VII

Determination of Americium Grown into Hanford Plutonium Product Samples

Sample no.	$\frac{MWD}{T}$	Time since separation, Days	Am found counts/min	Pu + Am counts/min
1	55	542	479	430,064
			475	
			475	
			472	
2	212	774	1747	428,340
			1730	
			1730	
			1713	
3	287	1108	5878	1,195,690
			6002	
			5817	
			5968	
4	287	1108	2547	622,930
			2615	
			2589	
			2599	
5	358	895	4126	629,869
			4065	
			4059	
			4081	
6	417	577	1699	311,330
			1697	
			1746	
			1715	
7	410	430	3576	868,032
			3566	
			3677	
			3748	
8	448	760	1455	194,638
			1488	
			1494	
			1458	

TABLE VII (contd.)

Sample no.	MWD/T	Time since separation, Days	Am found counts/min	Pu + Am counts/min
9	525	655	12216 12140 12447 12222	1,350,820
10	572	348	2957 2987 3119 3048	625,040
11	605	557	5714 5705 5911 5681	674,900
12	726	266	4479 4462 4475 4467	734,919
13	600	107	955 978 990 1014	491,276
14	600	107	1091 1084 1100 1088	513,419
15	600	106	1027 1015 992 987	501,315
16	600	107	1125 1126 1124 1133	526,083

The isotopic composition of each of the plutonium samples was measured; Pu-238 by alpha energy analysis, 240 by fission counting, and 239 by difference methods. These methods have been discussed in the section on analytical methods. The final isotopic composition of the samples and the "R" factor (ratio of the specific activity of pure Pu-239 to the specific activity of the samples) are given in Table 8. These data were taken from the report by Kinderman et al[25].

TABLE VIII

Isotopic Composition of Plutonium Samples

Sample no.	Pu-239 wt %	Pu-239 wt %	Pu-240 wt %	Pu-241 wt %	R
1	0.0020	99.068	0.904	0.026	0.9720
2	0.0033	98.18	1.78	0.040	0.9475
3	0.0041	97.75	2.17	0.075	0.9366
4	0.0042	97.62	2.31	0.063	0.9329
5	0.0051	97.095	2.778	0.122	0.9208
6	0.0055	96.67	3.16	0.158	0.9115
7	0.0061	96.319	3.44	0.159	0.9044
8	0.0056	96.571	3.26	0.168	0.9096
9	0.0073	95.80	3.96	0.237	0.8911
10	0.0039	95.54	4.22	0.235	0.8856
11	0.0081	95.30	4.43	0.264	0.8799
12	0.0010	94.36	5.24	0.394	0.8591
13	0.0084	95.11	4.56	0.323	0.8771
14	0.0084	95.01	4.65	0.332	0.8751
15	0.0086	94.92	4.76	0.313	0.8724
16	0.0084	94.93	4.73	0.334	0.8737

The abundances of plutonium-241 shown in the above table were calculated from the data of Tables 7 and 8 by means of the equation given in the section on analytical methods. In practice, approximate values for the plutonium-241 concentration were first calculated from the experimental data and "R" values neglecting the very small contribution of this isotope. The approximate plutonium-241 contents were then used to calculate a more accurate "R" value. Final values for the plutonium-241 abundance were then calculated again.

The weight percent of plutonium-241 in pile produced plutonium as a function of the total neutron irradiation in megawatt days per ton of uranium is shown in Figure 11. The exposure values were taken from process records in all cases and are estimated to be uncertain to about 10%.

DISCUSSION

The americium procedure developed for this problem offers a number of advantages over previous methods which recommend its future application. The solvent extraction procedure has been found to require only about thirty minutes for a determination, in comparison with the two to three hours required for the modified cerium fluoride method. Since americium frequently occurs in systems containing large amounts of fission products, operator exposure to intense beta and gamma radiation is appreciably reduced in the TTA method. The solvent extraction procedure does not require a carrier for americium, thus avoiding two analytical difficulties inherent in previous methods. The contamination of the precipitated americium with adsorbed plutonium in the cerium fluoride method has been mentioned. A second effect associated with the presence of relatively large amounts of inert carrier is the loss in counting rate due to self-absorption of the alpha particles in the body of precipitate. Both of these effects are avoided in a solvent extraction type of procedure in which the final sample is mounted in a carrier-free condition.

Two previous determinations of the distribution of americium into TTA-benzene solutions as a function of pH have been carried out by Werner and Perlman(26) and by Moore(27). The comparison of the data from these sources with the data of this paper is shown in Figure 12. Agreement between the various sources is within the experimental error of the investigations.

The determination of the half-life of plutonium-241 reported here was intended largely as a survey experiment to suggest the use of one of

FIGURE 11

Production of Pu-241 as a Function of Exposure

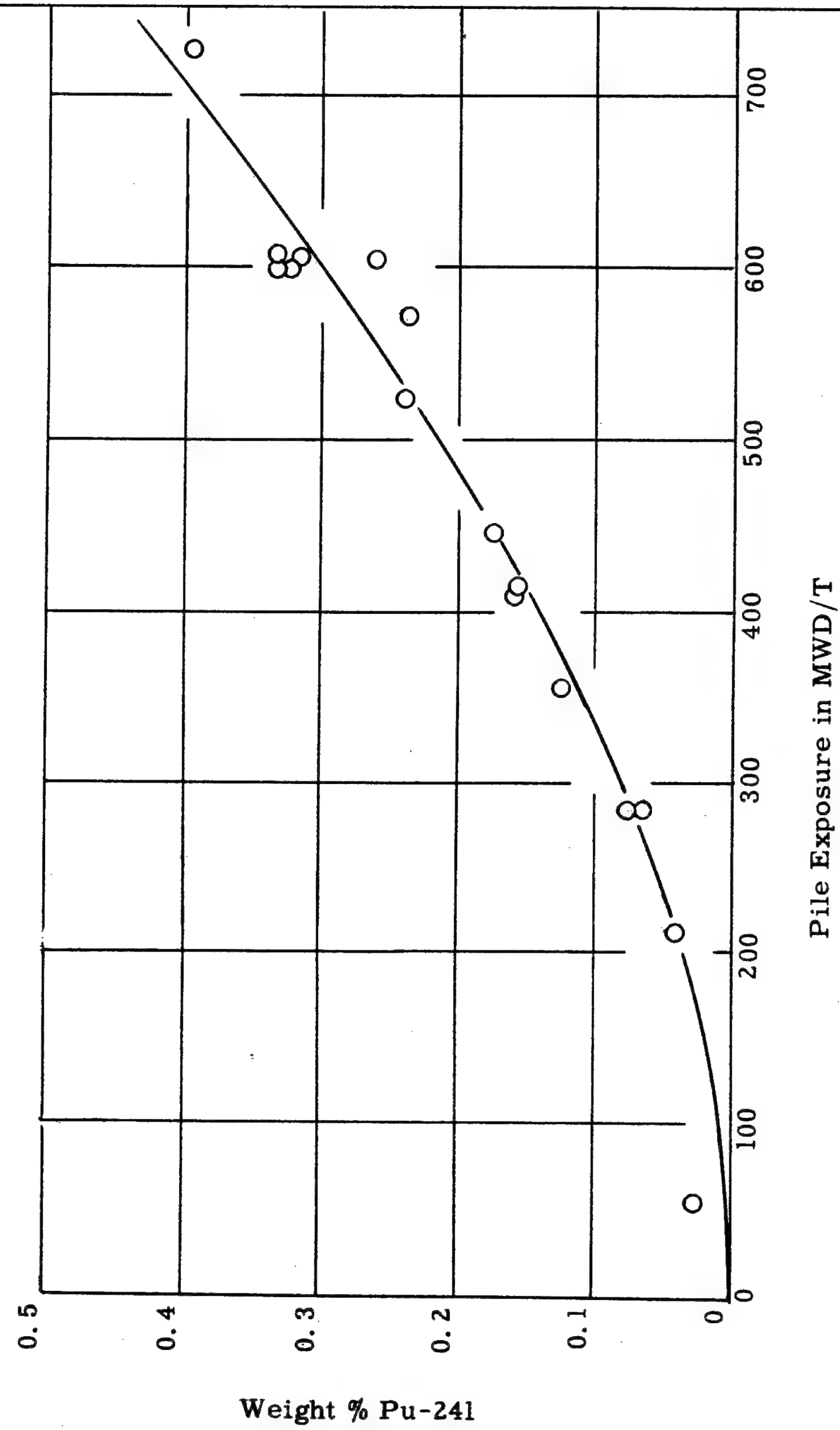
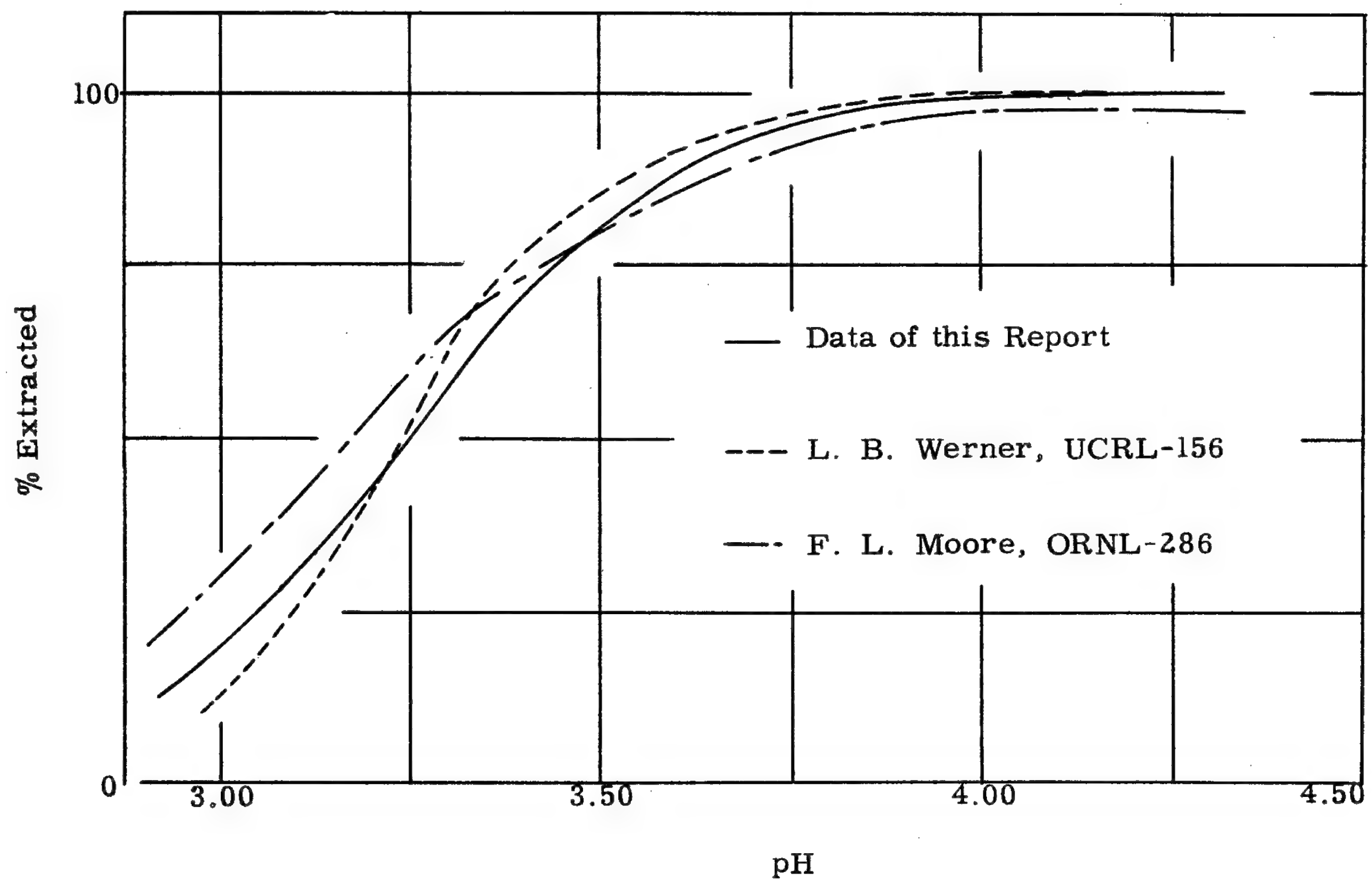


FIGURE 12

Extraction of Americium as a Function of pH

Comparison of Data



the several published values. The value found is subject to considerable uncertainty due to the precision of the measurements. On the basis of the results given in the experimental part of this paper, a value of 14.2 years was chosen for use in the plutonium-241 production studies.

Since exposure data are not available generally for the large number of plutonium samples for which isotope ratios have been determined by other workers, the relation between plutonium-240 and -241 is a better basis of comparison. The comparison of the data of this report with the theoretical predictions of Larrick are shown in Figure 13. Larrick's curve is consistently lower in plutonium-241 for the same amount of plutonium-240. This is very probably due to the choice of a 26,000 barn value for the total absorption cross section of the heavier isotope, leading to a large burn-out during the course of irradiation. More recent estimates of this cross section are in the neighborhood of 1500 barns(28), which value would bring the predicted curve in close agreement with the experimental data.

The very satisfactory agreement between the measurements of this report and the mass spectrographic and beta counting determinations of isotope ratios is illustrated in Figure 14. The mass spectrographic measurements were made on Pu from irradiated uranium and on irradiated plutonium itself(29). No significant difference is evident. The beta counting determinations were made by the direct measurement of the beta activity of a purified plutonium sample(30), the activity being assumed to be entirely from plutonium-241. No explanation for the consistently higher results for plutonium-241 can be readily adduced. Agreement with the mass spectrographic and americium growth data is good in any case.

As an aid in the prediction of the production of plutonium-241 as a function of exposure or plutonium-240 production, two algebraic expressions were developed from the experimental data. These relations are:

FIGURE 13

Pu-240 vs Pu-241

Comparison of Experimental and Theoretical Values

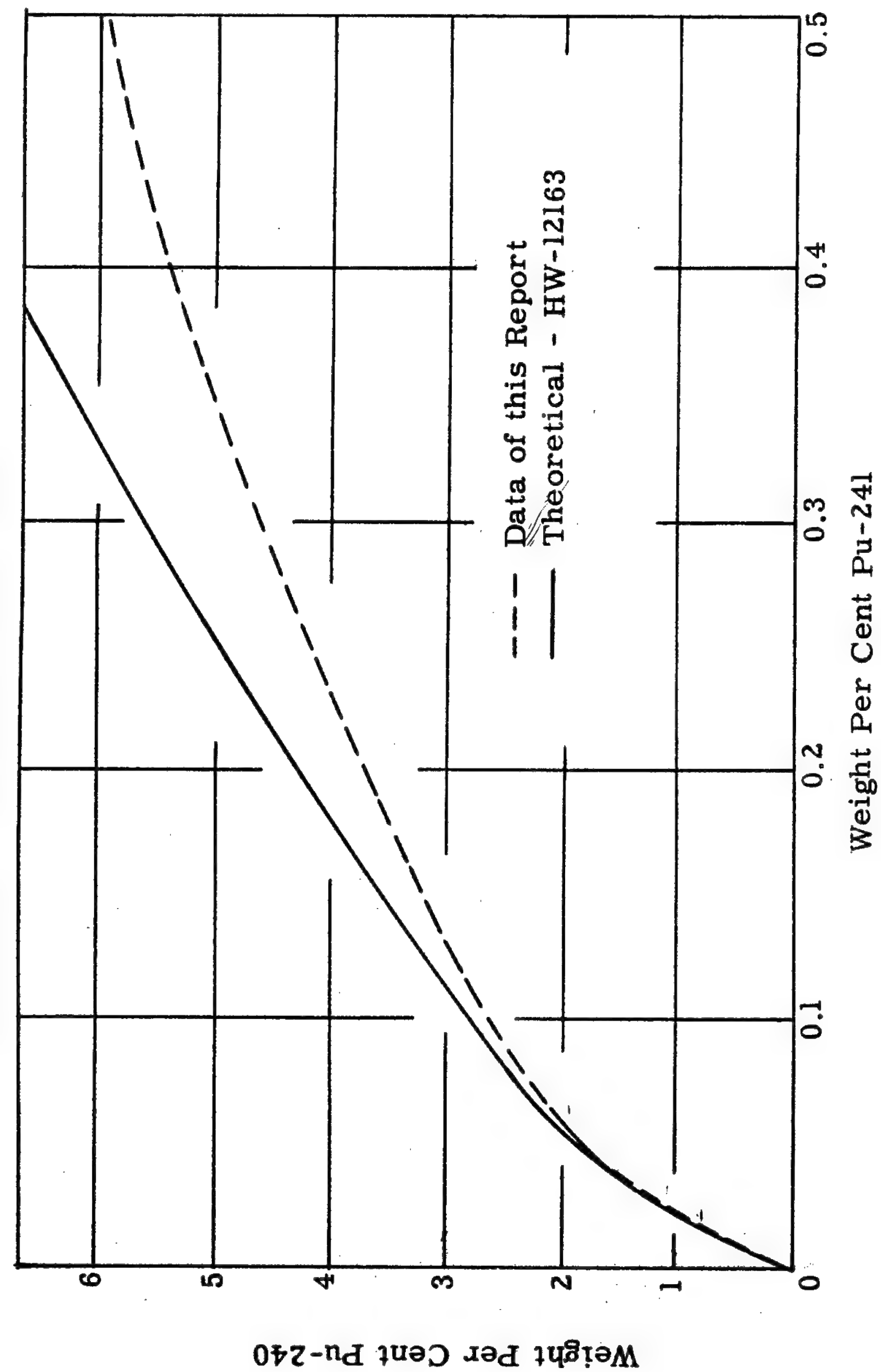
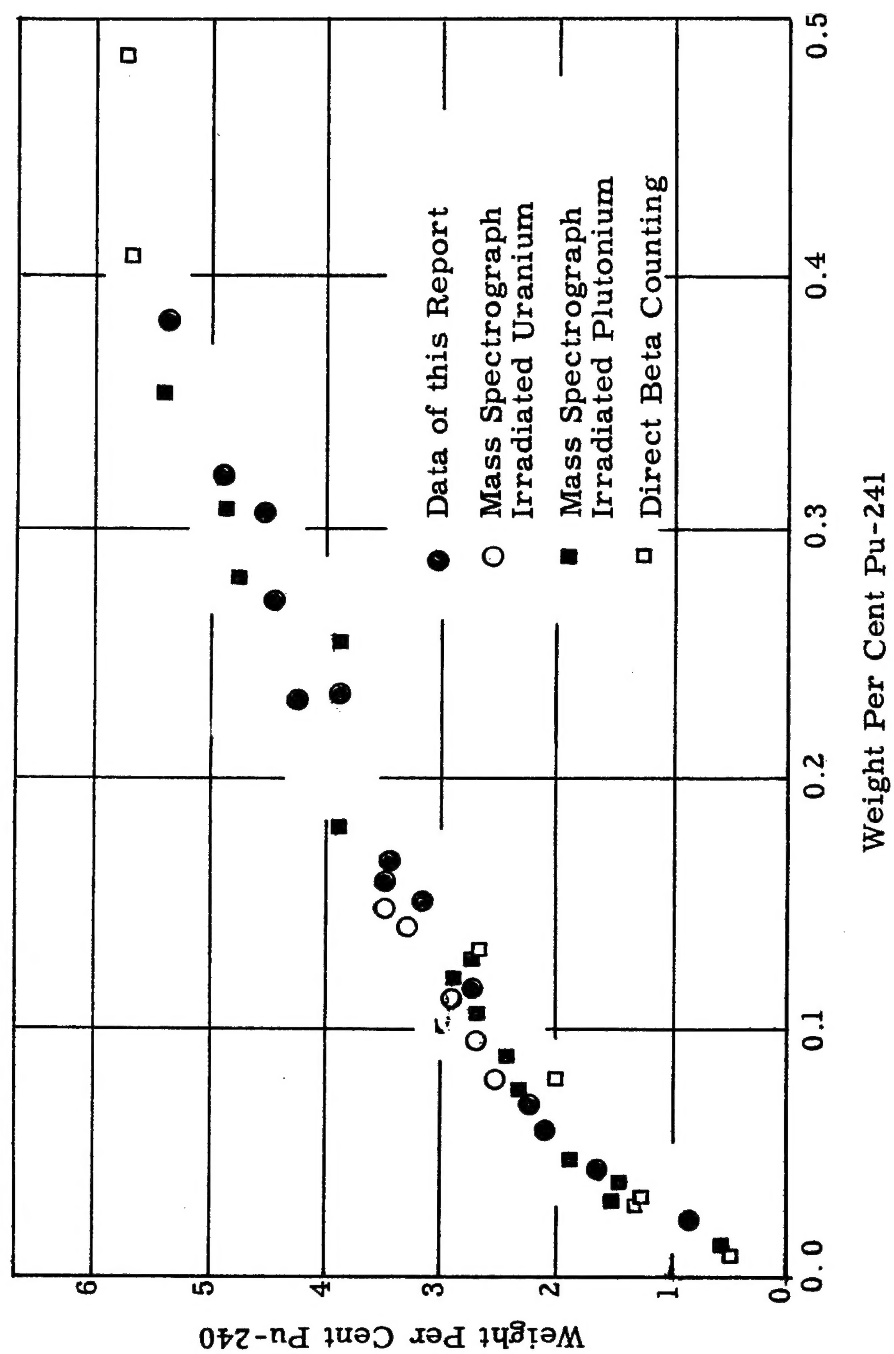


FIGURE 14

Pu-240 vs Pu-241. Comparison of Data



$$\text{(1)} \quad \text{Pu-241 Wt \%} = 3.708 \times 10^{-5} \text{ (MWD/T)} + 7.984 \times 10^{-7} \text{ (MWD/T)}^2$$

$$\text{(2)} \quad \text{Pu-241 Wt \%} = 0.01468 \text{ (Pu-240 Wt \%)}^2$$

These equations are of the form expected on theoretical grounds and closely represent the experimental data of this report.

ACKNOWLEDGMENTS

The author wishes to express his appreciation Drs. H. R. Schmidt and E. M. Kinderman for their encouragement and advice during the course of these investigations. The cooperation of Dr. S. G. Thompson of the University of California Radiation Laboratories in supplying us with the highly irradiated plutonium standard is gratefully acknowledged.

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